

CHAPTER I

INTRODUCTION



Acidity and basicity are paired concepts which are very often invoked to explain the catalytic properties of divided metal oxides and zeolites. Extensive investigations have been devoted to solid acid catalysts due to their great importance in petroleum chemistry. Studies concerning basic centers, in particular surface oxygens and hydroxyls, are far less advanced.

In view to establish correlation between catalytic activity and surface properties of catalysts, it is important to determine the number, nature, strength and location of the active sites. For that, a few number of physical and chemical methods have been developed. To estimate proton-accepting (basic) properties of the surface, two groups of methods can be used: titration with various reagents such as benzoic acid and spectral techniques. Among them, infrared spectroscopy, particularly for the study of adsorbates, is certainly the most commonly used.

While pyridine, ammonia and carbon monoxide are molecular probes commonly used in measurements of the acidity of metal oxides by IR spectroscopy, there is a lack of such probe molecules as far as metal oxide basicity is concerned. One of the most frequent approaches for characterizing basicity has been the use of adsorbed molecules, which act as spectroscopic probes. IR spectroscopy can then monitor specific perturbations of the adsorbed probe induced by interaction with the basic matrix. Lavelly (1996) has reviewed the subject of surface basicity characterization using adsorbed IR probes and concluded that there is no general probe molecule to characterize basic sites on solid bases.

Pyrrrole (C_4H_4NH) has been used as an acid probe of basic solids for several years. It is an amphoteric molecule, which interacts with the basic surface by a hydrogen bond between the NH group and the framework oxygens ($C_4H_4NH \cdots O$). The overall basic strength may then be obtained from the bathochromic shift of the

broad $\nu(\text{NH})$ stretching frequency. As a probe molecule, pyrrole possesses various advantages [Huang and Kaliaguine (1992)]. For example, its vapour pressure is convenient for studying adsorption from the vapour phase. Another important feature is probably its amphoteric character allowing it to interact with both basic (Lewis base) and acidic sites (Lewis and Brønsted acids). Generally, the adsorption of pyrrole on basic sites causes a relatively large bathochromic shift of its NH stretching frequency, because the hydrogen atom of the NH bond interacts directly with the basic sites. On the other hand, the adsorption on acid sites causes just a relatively small bathochromic shift in NH stretching frequency, because the acid sites interact with the pyrrole ring rather than the hydrogen atom of the pyrrole molecule. However, the characteristic IR band of pyrrole for basic sites was very weak due to the lower density of basic sites in these samples.

In the present work, pyrrole is used to measure the basicity and identify types of oxygen anion on surfaces in three types of catalysts by in-situ FTIR method and GC pulse technique: metal oxide, metal hydroxide and zeolite.

This work is arranged as follows:

Chapter II shows literature reviews over the surface basicity measurement by pyrrole adsorption.

Chapter III describes the theory of acid-base properties and the basicity measurement techniques.

Chapter IV presents the experimental systems.

Chapter V shows the experimental results of the characterization of catalysts by in-situ Fourier Transform Infrared (FT-IR) and Flame Ionization Detector (FID) technique.

In the last chapter, the overall conclusion of this work and some recommendations for any future works are presented.